Supporting Information

Triethanolamine-assisted photodeposition of non-crystalline Cu_xP nanodots for boosting photocatalytic H_2 evolution of TiO_2

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EXPERIMENTAL SECTION

SI-1 Photoelectrochemical measurements

Photoelectrochemical measurements are conducted on electrochemical analyzer (CHI660E, China) with Na_2SO_4 solution (0.5 M) as the electrolyte. The reaction system includes working electrode, Pt counter electrode, and AgCl reference electrode. The light source was provided by one UV light (365 nm, 3 W). The sample-loaded FTO glasses were used as working electrodes. Typically, the sample (10 mg) is uniformly mixed with a solution of absolute ethanol and Nafion D-520 (1:1) by ultrasonic. The obtained suspension was spread on the FTO glass and stored in 60 ℃ oven for 12 h. The LSV measurement was carried out by a bias range of -0.8 to -1.6 V. In addition, the frequency range was set in a range of 10^{-3}-10^{-6} Hz to measure the EIS. Transient photocurrent responses with time (*i*-*t* curves) were determined at +0.5 V bias potential during repeated ON/OFF illumination cycles under 3W-LED (365 nm, 80 mW cm^{-2}) as light source. Mott–Schottky plots are measured under a frequency of 1000 Hz in 0.5 M Na_2SO_4 aqueous solution.

SI-2 The AQE calculation

The apparent quantum efficiency (AQE) of Cu_xP/TiO_2(1wt%) photocatalyst is calculated via the following equation:

$$\mathrm{AQE}(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

$$= \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

The average power of the UV-light (four 3-W 365 nm) was 17 mW/cm^2. Hence, the AQE can be calculated to be 7.7 %.

Table S1 Preparation conditions of contrast experiments

Sample	TiO_2	$CuSO_4$ (0.1 M)[a]	NaH_2PO_2 (0.2 mol/L^{-1})	Irradiation time	H_2-evolution rate
A	**----**	0.317 ml	20 ml	60 min	0 μmol h^{-1}
B	200 mg	**----**	20 ml	60 min	2.8 μmol h^{-1}
C	200 mg	0.317 ml	**----**	60 min	3.1 μmol h^{-1}
D	200 mg	0.317 ml	20 ml	----	0 μmol h^{-1}
E	200 mg	0.317 ml	20 ml	60 min	93.5 μmol h^{-1}

[a] the $CuSO_4$ aqueous solution with the presence of TEOA, where the molar ratio of TEOA to $CuSO_4$ was about 7:1.

Table S2 Fluorescence Emission Lifetime and Relevant Percentage Data Fitted by a Three-Exponential Function

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Average lifetime (τ_a) (ns)
TiO_2	0.18	76.03	2.63	23.97	2.19
Cu_xP-ND/TiO_2(1wt%)	0.2	78.62	2.79	21.38	2.25

The above fitted parameters are acquired via the following tri-exponential formulas:

$$I_{(t)} = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3)$$

(1) $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$

(2) where I_0 is the baseline correction value, A_1, A_2 and A_3 represent the tri-exponential factors, and τ_1, τ_2, τ_3 and τ_a corresponding the lifetime in various stages (radiation, non-radiation and energy transfer) and average lifetime.

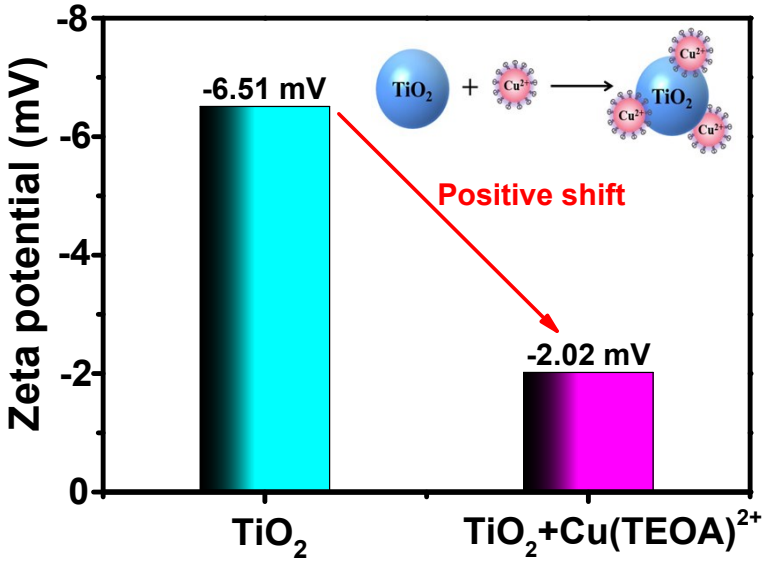

Fig. S1 Zeta potentials of TiO_2 before and after $Cu(TEOA)^{2+}$ modification.

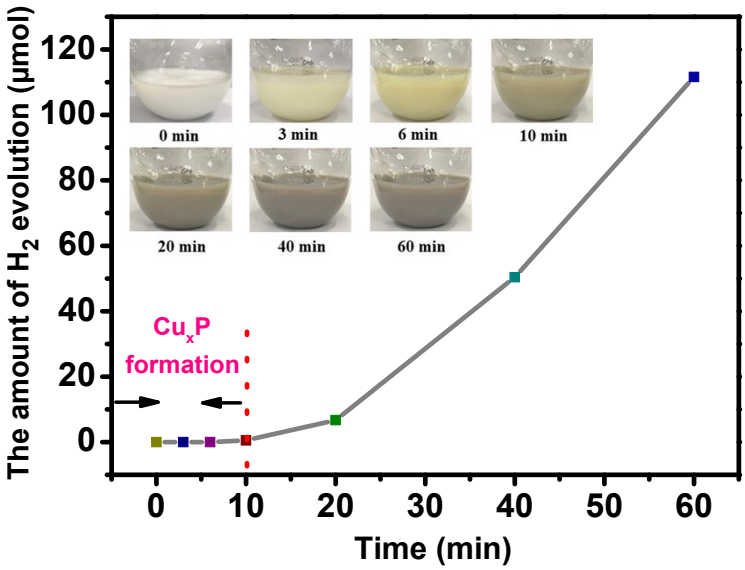

Fig. S2 Hydrogen production performance and color change during the photodeposition of Cu_xP/TiO_2(1wt%).

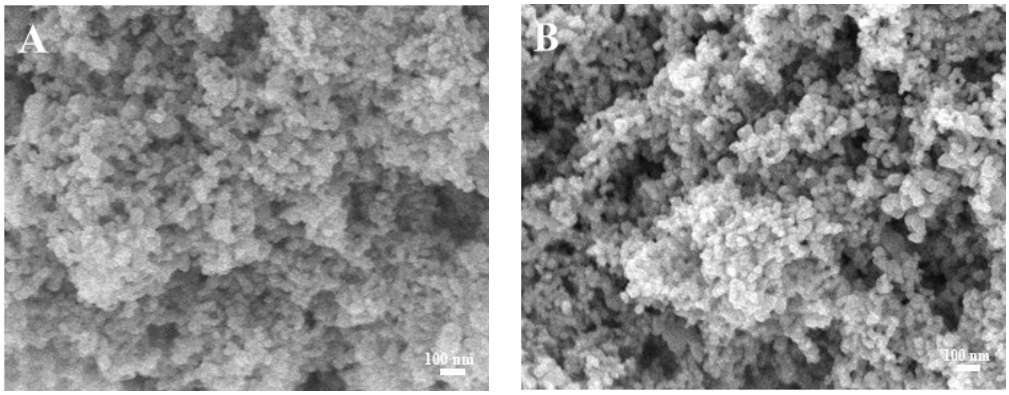

Fig. S3 FESEM images of (A) TiO_2 and (B) Cu_xP-ND/TiO_2(1wt%).

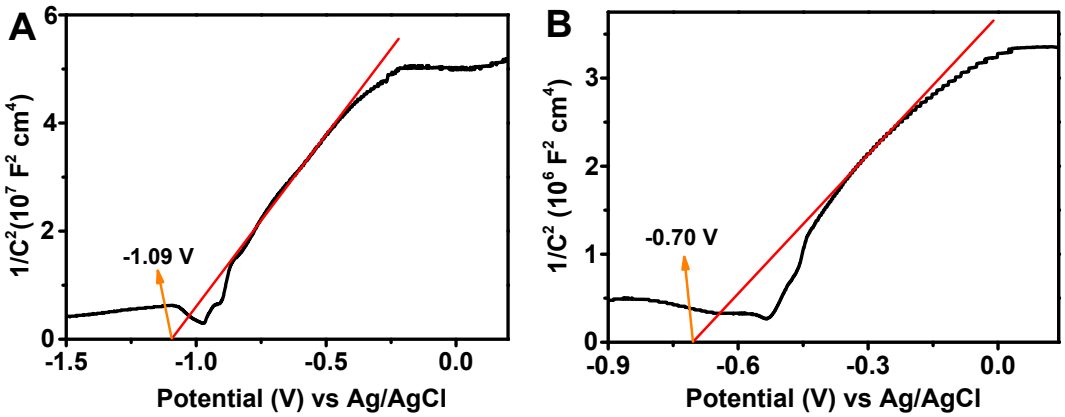

Fig. S4 Mott-Schottoy plots of (A) TiO_2 and (B) Cu_xP-ND/TiO_2(1wt%) in 0.5M Na_2SO_4 solution (pH = 7)

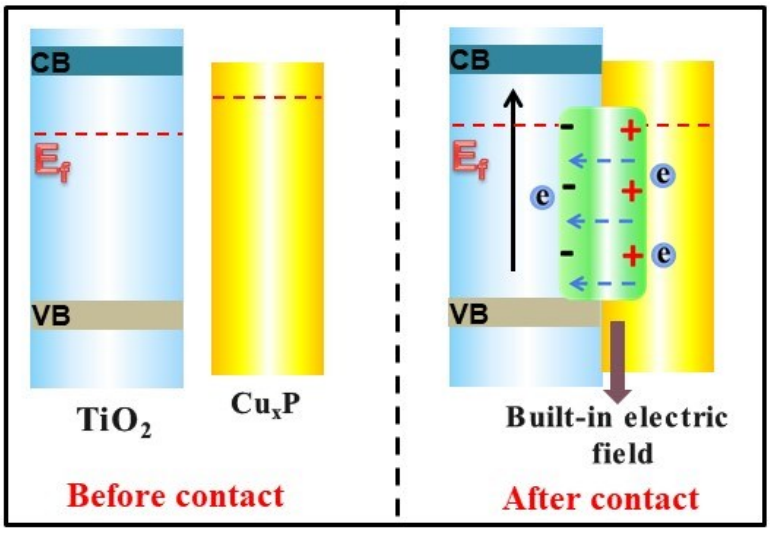

Fig. S5 Schematic illustration of electron transfer path before and after contact of TiO_2 and Cu_xP nanodots.